ANALYSIS OF THE SPECTRUM OF CH3OOH USING SECOND-ORDER PERTURBATION THEORY

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In this study, we calculate the spectrum of the OH stretch overtone region in CH_3OOH using vibrational second-order perturbation theory. Comparison of the calculated to the experimental spectra shows very good agreement. With this in place, the goal of this study is to use second-order perturbation theory to investigate the following questions. To begin with, we explored the origins of the transition strength and found that both mechanical and electrical anharmonicities contribute to the overall intensity. Then we studied the amount of OO stretch and OH stretch character in the wavefunctions that correspond to the states that are accessed by the experiment. This is of interest because the VMP (vibrationally mediated photodissociation) action spectrum of CH_3OOH is obtained by detection of the OH radical following vibrational excitation of the overtones/combination bands and the subsequent photodissociation along the OO bond. Interestingly, OH is detected in its vibrationless state following excitation of the OH and CH stretch overtones and combination bands involving the OH stretch. In contrast, vibrationally excited OH is only detected following excitation of OH stretch overtones in methyl peroxide. To further understand the origins of the intensity in CH_3OOH, we also explored the effects of deuteration in the OH and CH overtone regions.